UNITED STATES PATENT APPLICATION

FOR

CLEANING MASKS

INVENTORS:
SAMANTHA S.H. TAN
JIANQI WANG

PERKINS COIE LLP
CUSTOMER NUMBER: 22918
P.O. BOX 2168
MENLO PARK, CALIFORNIA 94026

ATTORNEY DOCKET NO.: 59081-8010.US01

EXPRESS MAIL NO.: EV 326 986 133 US

CLEANING MASKS

CLAIM OF PRIORITY

[0001] This application claims priority as a continuation-in-part to prior filed application number 10/627,416, entitled "Ultrasonic Assisted Etch Using Corrosive Liquids" and filed July 24, 2003, which is hereby incorporated by reference herein.

FIELD

[0002] The present invention relates to the field of semiconductor processing. More particularly, the present invention relates to cleaning masks used in semiconductor processing.

BACKGROUND

[0003] One form of semiconductor device utilizes C-bump technology for connection between the semiconductor device and external circuitry. To form the conductors utilized for C-bump technology, a mask is laid directly on a wafer of integrated circuits, and conductive metals are deposited on the integrated circuits at locations determined by the mask. C-bump technology allows for faster (higher frequency) connections between an integrated circuit and external circuit components (such as other integrated circuits or other devices). However, C-bump technology requires a complex and tightly controlled manufacturing process to achieve these results.

[0004] As may be expected, these masks have precise tolerances. In one process, holes in the mask are specified as 4 mils (101.6 μm) in diameter, with a tolerance of 1%. Moreover, each time the mask is used, it must then be cleaned, without changing the size

of the holes beyond the process tolerances. Understandably, cleaning the masks is a challenging problem.

[0005] Additionally, in some processes, the masks are to be used and cleaned multiple times, as many as 10 times per mask in some examples. Thus, a process of cleaning in which relatively small changes to holes in the mask would be useful. Moreover, semiconductor manufacturing plants are known to run 24 hours a day, 7 days a week. As a result, a fast cleaning process may be useful. Furthermore, cleaning the masks is an added expense to manufacturing. If cleaning expenses are too high relative to the replacement cost for a mask, cleaning may not be cost-effective. In some situations, cleaning a mask 10 times must cost less than the replacement cost of the mask for cleaning to be viable. As a result, an inexpensive cleaning process may be useful.

[0006] Figure 1 is an illustration of an embodiment of a prior art mask which may need to be cleaned. Mask 110 has numerous holes precisely placed to allow formation of conductive bumps on integrated circuits at desired location. In one embodiment, mask 110 is made of molybdenum, a relatively dense element. Holes 170 are placed at predetermined locations of mask 110, either in a regular array or at irregularly spaced intervals. In one embodiment, holes 170 are placed in a regularly-spaced array, with a spacing S between adjacent holes. In some embodiments, the spacing S may be expected to be about 120 μm, and each hole may be expected to be about 101.6 μm in diameter. Thus, cleaning of mask 110 may be a difficult and precise operation.

[0007] Figure 2 is the embodiment of a prior art mask of Figure 1 without material deposited thereon as seen in cross-section along line A-A. Mask 110 as illustrated in

Figure 2 has been cleaned of the materials deposited previously or is untouched. In one embodiment, D_1 after cleaning must be within 1% of D_1 before cleaning, or 101.6 μm +/- 1 μm. Moreover, in an alternate embodiment, D_1 after cleaning must be within 0.1% of D_1 before cleaning, or 101.6 μm +/- 0.1 μm to allow for up to 10 cleanings of mask 110. As illustrated, D_2 is the outer diameter of the hole, and may also have a similar tolerance for changes in diameter.

[0008] Figure 3 is an embodiment of a prior art mask having material deposited thereon as seen along line A-A in cross-section. Mask 110 is a mask designed to contact a semiconductor device for purposes of patterning conductors deposited on the semiconductor device. The illustration of Figure 3 is not to scale, but it may be expected that mask 110 will be a relatively thin, disc-shaped plate having numerous regularly-spaced and precisely placed holes therethrough.

[0009] In Figure 3, layers 120, 130, 140 and 150 are depicted as deposited on mask 110. Layer 120 is a chrome (Cr) layer which may be expected to adhere well to an integrated circuit. Layer 130 is a copper (Cu) layer which may be expected to conduct well. Similarly, layer 140 is a gold (Au) layer which may be expected to conduct well. Layer 150 is a lead/tin (Pb/Sn) solder layer which may be expected to both conduct well and bond well with external conductors.

[0010] These layers are deposited on the back side of a semiconductor in locations defined by holes through mask 110, such as the hole illustrated in the center of Figure 2 or 3. In one embodiment, the holes of mask 110 are specified to be 101.6 μm wide (as represented by D_1 of Figure 2), with a tolerance of 1%. Illustrated in Figure 4 is a cross-

sectional view of a prior art mask along line A-A after an improper cleaning of mask 110. Due to over-etching, D_1' is now too wide a diameter, and D_2' may also be too wide a diameter, thus taking mask 110 out of the prescribed tolerances for use in manufacturing. Such an improper cleaning would thus render mask 110 useless, and would potentially necessitate creation of a new mask before the manufacturing line in question could resume operation.

[0011] In general, cleaning or etching in semiconductor processes has been accomplished using a variety of materials or solvents, including various organic and inorganic acidic and alkali solutions. The desired etch rate, which allows for manufacturing in a reasonable time without over-etching but still achieves the objective (such as actually cleaning the mask) may be difficult to predict without experimentation. Various acids or bases may work well with some metals but poorly with other metals due to reactions between the etching ions and the metal to be cleaned.

[0012] Moreover, assisted etching is sometimes used, although that brings with it concerns about corrosive vapors arising out of the etching baths, as the energy added during assisted etching may result in more energetic atoms and turbulence at the surface of an etch bath, and a corresponding increase in airborne material from the etch bath. Of note, one process involves etching using an acid with electrolysis for assistance. Unfortunately, this requires care in selecting the metals to etch, as electroplating and exothermic reactions may occur depending on the relationships between the metals involved. Electroplating risks strengthening the bond which cleaning would normally break, and exothermic reactions raise safety concerns. Choosing the correct type of

solvent and the correct method of assistance (if any) for a given etching process is not a simple or obvious task.

SUMMARY

[0013] A method and apparatus for cleaning masks is described. In one embodiment, the invention is a method of cleaning a mask. In some embodiments, the invention includes placing the mask in an etching solution and agitating the solution to etch away materials deposited on the mask. In other embodiments, the invention includes a first vessel with an etching solution, a second vessel holding the first vessel within a second solution, and an agitator coupled or connected to the second vessel. In yet other embodiments, the invention includes placing the mask in an etching solution to etch away materials deposited on the mask, and may also include periodically scrubbing the mask.

[0014] In one embodiment, the invention is a method of cleaning a molybdenum mask having a series of metals deposited thereon. The method includes placing the molybdenum mask in a cleaning solution including hydrochloric acid. The method also includes removing the molybdenum mask from the cleaning solution after a predetermined period of time. The molybdenum mask may have a set of through holes.

[0015] In another embodiment, the invention is an apparatus for cleaning masks. The apparatus includes a first vessel having an open top. The apparatus also includes a second vessel having an open top, the second vessel containing the first vessel. The apparatus further includes an agitator within the second vessel. Alternatively, the agitator may be coupled to the second vessel or contacting the exterior of the second vessel.

[0016] In an alternate embodiment, the invention is a method of cleaning a mask. The method includes placing the mask in a cleaning solution. The method also includes agitating the cleaning solution at a predetermined agitation level for a predetermined period of time.

[0017] In still another alternate embodiment, the invention is an apparatus for cleaning masks. The apparatus includes a first means for cleaning the masks. The apparatus includes a second means for holding the masks. The apparatus also includes a third means for agitating the first means and the second means. The apparatus further includes a fourth means for containing the first means. The apparatus also includes a fifth means for surrounding the fourth means. Moreover, the apparatus includes a sixth means for holding the fifth means and the third means.

[0018] In yet another alternate embodiment, the invention is a method of cleaning a mask. The method includes putting the mask in a container. The method also includes placing the container in a cleaning solution. The cleaning solution is contained within a first vessel. The first vessel is contained within a second vessel. The second vessel contains an aqueous solution surrounding the first vessel.

[0019] In still another alternate embodiment, the invention is a method of cleaning a molybdenum mask having a series of metals deposited thereon. The invention includes placing the molybdenum mask in a cleaning solution. The method also includes removing the molybdenum mask from the cleaning solution after a predetermined period of time. The method may further include agitating the cleaning solution at a

predetermined agitation level for a predetermined period of time. The series of metals may include chrome, copper, gold and a lead/tin mixture.

BRIEF DESCRIPTION OF THE DRAWINGS

[0020] The accompanying drawings, which are incorporated in and form a part of this specification, illustrate embodiments of the invention and, together with the description, serve to explain the principles of the invention. The drawings should be understood as illustrative of the invention, rather than restrictive.

[0021] Figure 1 is an embodiment of a prior art mask.

[0022] Figure 2 is the embodiment of a prior art mask of Figure 1 seen through the cross-section at line A-A without material deposited thereon.

[0023] Figure 3 is another illustration of the embodiment of a prior art mask of Figure 1 seen through the cross-section at line A-A with material deposited thereon.

[0024] Figure 4 is the embodiment of a prior art mask of Figure 1 seen through the cross-section at line A-A after material is improperly cleaned off.

[0025] Figure 5 is an embodiment of a cleaning system.

[0026] Figure 6 is an embodiment of a wafer holder holding a mask as seen along line B-B of Figure 5.

[0027] Figure 7 is another illustration of the embodiment of a wafer holder as seen along line C-C of Figure 6.

[0028] Figure 8 is yet another illustration of the embodiment of a wafer holder in perspective view.

[0029] Figure 9 is an embodiment of a process of cleaning a mask.

[0030] Figure 10 is an alternate embodiment of a process of cleaning a mask.

DETAILED DESCRIPTION

[0031] A method and apparatus for cleaning masks is described. In the following description, for purposes of explanation, numerous specific details are set forth in order to provide a thorough understanding of the invention. It will be apparent, however, to one skilled in the art that the invention can be practiced without these specific details. In other instances, structures and devices are shown in block diagram form in order to avoid obscuring the invention.

[0032] In some embodiments, the invention includes placing the mask in an etching solution and agitating the solution to etch away materials deposited on the mask. In other embodiments, the invention includes a first vessel with an etching solution, a second vessel holding the first vessel within a second solution, and an agitator coupled or connected to the second vessel. In yet other embodiments, the invention includes placing the mask in an etching solution to etch away materials deposited on the mask, and may also include periodically scrubbing the mask.

[0033] In one embodiment, the invention is a method of cleaning a molybdenum mask having a series of metals deposited thereon. The method includes placing the molybdenum mask in a cleaning solution including hydrochloric acid. The method also includes removing the molybdenum mask from the cleaning solution after a predetermined period of time. The molybdenum mask may have a set of through holes.

[0034] In another embodiment, the invention is an apparatus for cleaning masks. The apparatus includes a first vessel having an open top. The apparatus also includes a

second vessel having an open top, the second vessel containing the first vessel. The apparatus further includes an agitator within the second vessel. Alternatively, the agitator may be coupled to the second vessel or contacting the exterior of the second vessel.

[0035] In an alternate embodiment, the invention is a method of cleaning a mask. The method includes placing the mask in a cleaning solution. The method also includes agitating the cleaning solution at a predetermined agitation level for a predetermined period of time.

[0036] In still another alternate embodiment, the invention is an apparatus for cleaning masks. The apparatus includes a first means for cleaning the masks. The apparatus includes a second means for holding the masks. The apparatus also includes a third means for agitating the first means and the second means. The apparatus further includes a fourth means for containing the first means. The apparatus also includes a fifth means for surrounding the fourth means. Moreover, the apparatus includes a sixth means for holding the fifth means and the third means.

[0037] In yet another alternate embodiment, the invention is a method of cleaning a mask. The method includes putting the mask in a container. The method also includes placing the container in a cleaning solution. The cleaning solution is contained within a first vessel. The first vessel is contained within a second vessel. The second vessel contains an aqueous solution surrounding the first vessel.

[0038] In still another alternate embodiment, the invention is a method of cleaning a molybdenum mask having a series of metals deposited thereon. The invention includes placing the molybdenum mask in a cleaning solution. The method also includes

removing the molybdenum mask from the cleaning solution after a predetermined period of time. The method may further include agitating the cleaning solution at a predetermined agitation level for a predetermined period of time. The series of metals may include chrome, copper, gold and a lead/tin mixture.

[0039] Figure 5 is an embodiment of a cleaning system. After some experimentation, it has been determined that mask 110 and similar masks may be cleaned using an etching solution, and assisted etching may be useful. First or inner vessel 310 contains an etching solution 320 and is covered by cap 330. Within inner vessel 310, wafer boat 340 is placed, and wafer boat 340 holds masks such as mask 110. Preferably, wafer boat 340 holds several masks at a time, while allowing fluid to contact the surfaces of the masks.

[0040] Inner vessel 310 rests on a base 360 placed at the bottom of outer or second vessel 350. Vessel 350 contains aqueous solution 370 and may be covered by cap 380. Outer vessel 350 rests on agitator 390, which may be a slab attached to a vibrating mechanism for example. Thus, etching or cleaning solution 320 may be agitated through use of agitator 390, vibrations of which will be communicated through vessel 350, base 360, and vessel 310. Agitator 390 may be rated based on a frequency of vibrations or based on power output through vibrations.

[0041] Figure 6 is an embodiment of a wafer holder holding a mask as seen along line B-B of Figure 5. The wafer holder 410 may be used as part of wafer boat 340 of Figure 3, for example. Wafer holder 410 includes protrusion 420, latch 430 and hinge portion 440. In one embodiment, wafer holder 410 is made of Teflon ®. In an alternate embodiment, wafer holder 410 is made of a high-density polyethylene. In either

embodiment, wafer holder 410 may be expected to have a groove (such as a v-shaped groove) into which a mask 110 may fit. Such grooves may be along one or more inner surfaces of wafer holder 410, allowing for a snug fit and secure enclosure of a mask to prevent bending of the mask.

[0042] Figure 7 is another illustration of the embodiment of a wafer holder as seen along line C-C of Figure 6. Groove 450 is shown as part of an inner surface of wafer holder 410. Figure 8 is yet another illustration of the embodiment of a wafer holder in perspective view. Wafer holder 410A (including protrusion 420A, latch 430A and hinge 440A) is connected to a second wafer holder 410B (including protrusion 420B, latch 430B and hinge 440B). Together, wafer holders 410A and 410B make up all or a portion of a wafer boat such as wafer boat 340. Note that the exact shape of wafer holder 410 may be varied in many ways while remaining within the spirit and scope of a wafer holder.

[0043] The cleaning system and wafer holders may be used in various ways. Figure 9 is an embodiment of a process of cleaning a mask. At block 510, a mask to be cleaned is received, such as from a manufacturing line. At block 520, the outer vessel of a cleaning system or apparatus is filled, such as with deionized water. At block 530, the inner vessel of the cleaning apparatus is filled, such as with an etching solution, and the inner vessel is placed within the outer vessel. At block 540, the mask is placed within a container, such as a mask or wafer holder. At block 550, the container is placed within the inner vessel, thereby submerging the mask in the etching solution. At block 560, the

inner vessel is covered, thereby reducing fumes or escaping molecules of the etching solution.

[0044] At block 570, the cleaning system is agitated, introducing energy into the system and potentially speeding up the etch rate of the etching solution. After a predetermined amount of time, at block 580, the container is removed from the inner vessel. At block 590, the masks are washed with de-ionized water. At block 595, the masks are dried with nitrogen. Thus, masks free of materials previously deposited thereon are produced.

[0045] Note that agitation need not be used. Figure 10 is an alternate embodiment of a process of cleaning a mask. At block 610, a mask to be cleaned is received, such as from a manufacturing line. At block 620, the outer vessel of a cleaning system or apparatus is filled, such as with deionized water. At block 630, the inner vessel of the cleaning apparatus is filled, such as with an etching solution. The inner vessel is placed within the outer vessel, or may already be affixed there. At block 640, the mask is placed within a container, such as a mask or wafer holder. At block 650, the container is placed within the inner vessel, thereby submerging the mask in the etching solution.

[0046] At block 655, the inner vessel is covered, thereby reducing fumes or escaping molecules of the etching solution. After a predetermined amount of time, at block 660, the inner vessel is opened or uncovered, allowing access to the masks. At block 665, the container is removed from the inner vessel. At block 670, the masks are scrubbed, removing any film (such as a protective or passivating coating) which may have formed.

At block 675, a determination is made as to whether the masks are clean. If not, the process returns to block 650, and the container is placed in the inner vessel again.

[0047] If the masks are clean, at block 680, the masks are washed with de-ionized water. At block 690, the masks are dried with nitrogen. Thus, masks free of materials previously deposited thereon are produced. Note that various different etching solutions may or may not require scrubbing or agitation, and that different times may be appropriate, depending on the materials deposited on the mask.

EXAMPLE 1

[0048] In one embodiment, an etching solution of hydrochloric acid (HCl) was used. Various concentrations of hydrochloric acid, ranging from approximately 10% to approximately 37% by weight were tested. It was found that a concentration of approximately 37% was particularly useful with agitation. Etching with the 37% concentration and an agitation power of about 25 W/gallon of liquid for about 20 minutes quickly removed materials deposited on the mask with relatively minimal damage to the mask (within the +/- 0.1 μm specification). Damage to the masks was inspected on an SEM (scanning electron microscope).

[0049] Various different power settings for the agitator were tried, ranging from about 5 W/gallon of liquid to about 50 W/gallon of liquid. Agitation power may be used at levels even higher, such as 100 W/gallon for example. Similarly, etching times were tested, ranging from just a few minutes to 40 or more minutes, and temperatures were tested, ranging from about room temperature (25 °C) to about 40 °C.

EXAMPLE 2

[0050] In an alternate embodiment, an etching solution of hydrochloric acid was used. The hydrochloric acid was found to be most useful at a weight concentration of about 37%. No agitation was used. It was found that the Pb/Sn layer tended to bond with chloride to form an insoluble substance, such that the masks took significantly more than 20 minutes (on the order of 20 hours in one instance) to achieve a clean etching.

EXAMPLE 3

[0051] In another alternate embodiment, an etching solution of hydrochloric acid was used. The hydrochloric acid was found to be most useful at a weight concentration of about 37%. No agitation was used. It was found that the Pb/Sn layer tended to bond with chloride to form an insoluble substance, such that the masks needed to be scrubbed repeatedly to achieve a clean etching. The entire process was found to take significantly more than 20 minutes, but less than 20 hours.

EXAMPLE 4

[0052] In yet another alternate embodiment, an etching solution of hydrochloric acid and acetic acid was used. The hydrochloric acid was found to be most useful at a weight concentration of about 99% of the total acid in the etching solution, although weight percentages as low as 90% (9:1, hydrochloric acid to acetic acid) were tested. No agitation was used. It was found that the Pb/Sn layer tended to bond with chloride, such that the masks took significantly more than 20 minutes (on the order of 20 hours in one instance) to achieve a clean etching.

OTHER EXAMPLES

[0053] Various other etching solutions were attempted. These included nitric acid (HNO_3), phosphoric acid (H_2PO_4), hydrofluoric acid (HF), sodium hydroxide (NaOH), sulfuric acid (H_2SO_4), and hydrogen peroxide (H_2O_2). Furthermore, electrolysis (use of an electric field between the masks and an electrode in the solution) was used in conjunction with various bases. These acids and bases had differing results for the specific combination of metals used, and some showed potential to be useful with different combinations of metals. The concentrations ranged from about 5% to about 99.9%, with various concentrations tested for each acid. Some ranges of concentrations tested are included in the following table:

Acid	Concentration Range
Nitric Acid	7% - 70%
Acetic Acid	13% - 99.9%
Phosphoric Acid	40% - 86%
Sodium Hydroxide	5-10% (electrolysis)
Sulfuric Acid	30% - 96%
Hydrofluoric Acid	5% - 49%
Hydrogen Peroxide	5% - 30%

[0054] Each of these acids was found to have varying degrees of effectiveness. Note that the agitation can be measured or set as a function of frequency of vibration, and frequencies in the range of 25-40 kHz were found to be particularly useful. Also, note that the wafer boats can be formed in a variety of ways, and both a boat and top design and a clamshell design are potentially useful.

[0055] From the foregoing, it will be appreciated that specific embodiments of the invention have been described herein for purposes of illustration, but that various modifications may be made without deviating from the spirit and scope of the invention. In some instances, reference has been made to characteristics likely to be present in various or some embodiments, but these characteristics are also not necessarily limiting on the spirit and scope of the invention. In the illustrations and description, structures have been provided which may be formed or assembled in other ways within the spirit and scope of the invention. Similarly, methods have been illustrated and described as linear processes, but such methods may have operations reordered or implemented in parallel within the spirit and scope of the invention. Accordingly, the invention is not limited except as by the appended claims.